

## Chapter 5

# **First steps towards application of the fs laser induced dichroism in composite glass with spherical Ag nanoparticles**

In Chapter 3, we considered SP assisted modifications of the single spherical Ag nanoparticles embedded in soda-lime glass upon exposure to intense 150 fs laser pulses. The experimental data are indicating that the polarization dependent elongation of the shape of metal clusters is responsible for the laser induced dichroism in the composite glass. However, the linear and nonlinear optical properties of the composite medium caused by the SP resonance are strongly dependent on the host matrix, size, and shape as well as on distribution of the metal clusters. These factors could apparently affect the shape transformation processes induced by fs laser pulses. In this chapter, we will study the fs laser modifications in soda-lime glass with inhomogeneous distribution of the Ag nanoparticles. For instance, the opportunity of three-dimensional (3D) anisotropic structuring in samples with a fill factor gradient of silver clusters in the depth by multicolour irradiation with fs laser pulses. The idea is based on a selective wavelength excitation of Ag nanoparticles with proper fill factor, which in turn defines the spectral width and position of SP band. On the other hand, multicolour irradiation of such type of samples and subsequent laser modifications allow production of high contrast dichroic filters. This aspect will also be described in this chapter too. One should be noticed that in contrast with the samples containing aggregated Ag nanoparticles (filling factor about of 0.7) studied in previous chapter, experiments presented here were performed on the samples with maximal filling factor about of 0.3 near to the surface and decreasing in the depth. In spite of the considerable inhomogeneous broadening of the SP band caused by multipolar interactions between nanospheres, the distance between them is still longer than the size of the single particle. Thus, the induced dichroism presented in this chapter should be referred to as modification of the separated silver nanoparticles. Proposed techniques could be used in manufacturing of different 3D, polarization and wavelength selective micro-devices such as polarizers, filters, gratings, displays and rewriting optical data storage devices.

### 5.1. 3D anisotropic structuring in the glass with filling factor gradient of Ag nanoparticles in the depth.

As it has been shown in the Section 2.5, composite glass with Ag nanoparticles distributed near to the surface of the sample with fill factor gradient in the depth reveals the dependence of the absorption spectra on the depth. This opens a way for the wavelength selective excitation and modification of the nanoparticles with proper filling factor by fs laser pulses.

Irradiation of the samples was performed in multi-shot mode at three different wavelengths: by linearly polarized pulses at 400 nm derived from second harmonic generator (SHG), also 500 nm and 550 nm generated by optical parametric amplifier (OPA) with following sum frequency of signal and fundamental wavelength at 800nm. In each case, pulses with energy up to 20  $\mu$ J and temporal width of 150 fs were focused on the sample using a lens with focal length of 300mm yielding to a spot diameter of approximately 150 $\mu$ m. The sample was mounted on a motorized X-Y translation stage with its glass surface towards the incident beam. In each case square areas of approximately 3x3 mm<sup>2</sup> were written on the sample using multi shot

regime of the laser with a pulse density of approximately  $2 \times 10^4$  shots/mm<sup>2</sup>.

Under these conditions, irradiation of the samples by fs laser pulses resulted in similar changes of the extinction spectra as in the case of single nanoparticles (Chapter 3), i.e. splitting of the SP band and red-shift of the p-polarized band. However, in contrast to samples with low fill factor now also the longer laser wavelengths 500 nm and 550 nm caused strong spectral changes responsible for dichroitic coloration (Fig.5.1). In other words, a wavelength dependent dichroism is produced. Here we have to notice that irradiations of the samples were carried out from the glass substrate side as it is

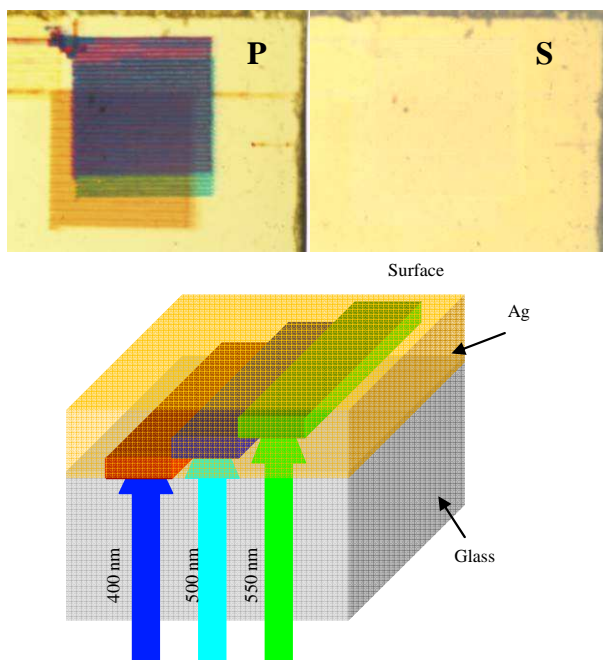


Fig.5.1 The glass sample with Ag nanoparticles irradiated at 400 nm (red), 500 nm (blue) and 550 nm (green) by 150 fs laser pulses. Images for p- and s-polarizations. Bottom: scheme of the sample irradiation.

shown in bottom of the Fig.5.1.

As is seen in Fig.5.2 (giving the p-polarized spectra), irradiation at  $\lambda = 400$  nm leads to the appearance of a SP band (seen as shoulder) at 470 nm, irradiation at 500 nm results in a band peaked at 570 nm, and irradiation at 550 nm produces a SP band at 660 nm. Here apparently the observed different red-shift of the SP peaks after irradiation at different wavelengths has to be explained by a combination of different aspect ratio of the particles and different dipol-dipol interactions between ellipsoids in different depths (i.e., at different fill factor). In all three cases there remains a strong absorption band close to 400 nm, indicating that a considerable part

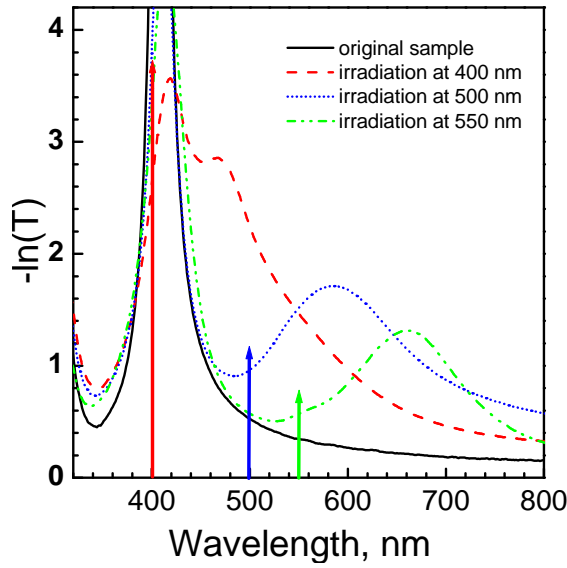


Fig.5.2 Extinction spectra (measured with light polarized parallel to the laser polarization) of original glass sample containing Ag nanoparticles with fill factor gradient; original spectrum (solid curve) and spectra after irradiation by fs laser pulses at  $\lambda = 400$  nm (dashed), 500 nm (dotted) and 550 nm (dash-dotted).

we define for the SP bands created by the different irradiation wavelengths a polarization contrast  $P$  given as the value of the peak absorption constant  $A_{\max}(\lambda)$  of the difference extinction spectra ( $A(\lambda) = \alpha_p(\lambda) - \alpha_s(\lambda)$ ), where  $\alpha$  denotes the usual absorption constant. This value  $P$  is closely

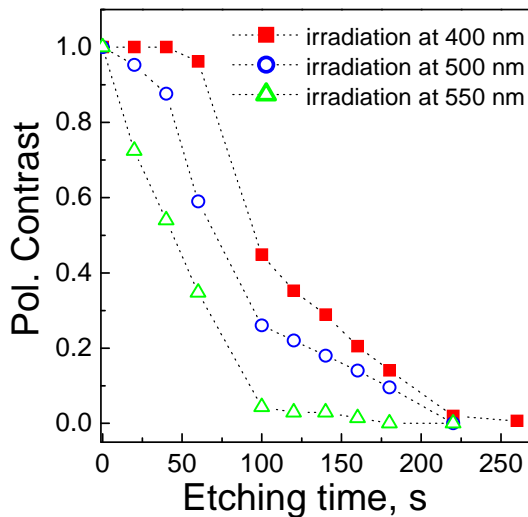


Fig.5.3 Evolution of Polarization contrast  $P$  (see text for definition) as a function of etching time in 12% HF acid, determined for three different sample regions, which were irradiated by fs laser pulses at  $\lambda = 400$  nm (squares), 500 nm (circles) and 550 nm (triangles).

of the silver nanoparticles has not been deformed to non-spherical shape. This can be taken as evidence for an inhomogeneous broadening of the SP band caused by the fill factor gradient of Ag nanoparticles (see Chapter 2), and for the possibility to deform particles in different depths selectively by irradiation of laser wavelengths adjusted to the SP band position (and thus fill factor) in that depth.

A second, direct proof for the modifications being located in different depths was obtained by etching of the sample in 12% HF acid and monitoring in a time interval of 20 seconds separately the extinction spectra of that etched areas, which had before been modified by irradiation at 400, 500, or 550 nm wavelength.

For convenience of presentation, we define for the SP bands created by the different irradiation wavelengths a polarization contrast  $P$  given as the value of the peak absorption constant  $A_{\max}(\lambda)$  of the difference extinction spectra ( $A(\lambda) = \alpha_p(\lambda) - \alpha_s(\lambda)$ ), where  $\alpha$  denotes the usual absorption constant. This value  $P$  is closely correlated with the anisotropic SP extinction bands of modified Ag nanoparticles with oblong shape (and uniform orientation), and can thus be used as an indicator for the content of such modified particles in the sample. Fig.5.3 gives the values we obtained during etching for the 3 different areas, normalized to the same starting value, as a function of etching time. Clearly the fading of the polarization contrast depends strongly on the excitation laser wavelength. While, e.g., the content of the Ag nanoparticles modified by irradiation at 550 nm has decreased by 50% already within the first 50 seconds, the polarization contrast  $P$  of the areas irradiated at 400 nm and 500 nm is almost unchanged after that time. The content of Ag nanoparticles modified at 500 nm (400 nm) reaches the level of 50%

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only after 75 s (100 s). In other words, irradiation at 550 nm affects mostly Ag nanoparticles with the highest fill factor, which are located near to the surface of the sample (see a picture in bottom of the Fig. 5.1), irradiation at a wavelength of 500 nm results in modifications in an intermediate region in larger distance from the sample surface, and the changes in extinction spectra induced by excitation at 400 nm are caused by modifications in the deepest layer (with respect to the sample surface) where collective interactions between Ag nanoparticles are negligible. It should be noted that this interpretation corresponds well with the visual impression which can be observed using a conventional stereo microscope.

It was tried also to irradiate the sample from the side containing Ag nanoparticles, as opposed to the irradiation from the glass substrate side used for all experiments described above. This approach did not lead to the same results, mostly because of the significant losses for each excitation wavelength caused by the broad absorption band of the upper layers with a high fill factor of Ag nanoparticles (compare Section 2.5, the Fig.2.12). Thus, in the case of irradiation onto the particle containing side one has to increase considerably the intensity of the laser pulses in order to increase the penetration depth of the laser light into the sample. This, however, results in spectral changes mostly in the upper layer preventing the selective modifications in the depth obtained by irradiation through the neat glass side. On the other hand, in the Section 5.3 of this chapter it will be shown how multicolor exposure from the layer side can be used for producing of high contrast wavelength selective dichroic filters.

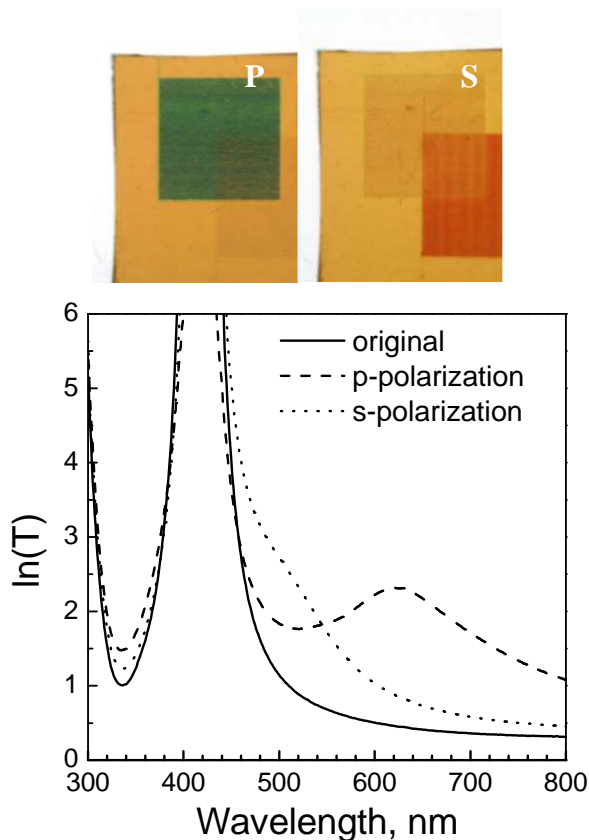


Fig. 5.4 Irradiation of the samples with Ag nanoparticles at 400 nm and 550 nm in crossed polarizations: in top – image of the sample in polarized light; bottom – polarized extinction spectra of overlapping area between irradiated fields on the sample.

It is obvious that presented technique has a large potential for a number of applications including 3D micro-structured, dichroic optical devices or optical 3D data storage, which in turn will be discussed in the next section. In this context it is important to notice that the sequence of irradiation wavelengths of the fs laser pulses should be done in the direction of wavelength decrease (550 nm, 500 nm, 400 nm), since otherwise, due to the red-shifted SP band (p-polarization) of the deformed oblong nanoparticles, the modifications in the deeper layer will be partially ‘destroyed’ by the laser pulses at longer wavelengths necessary to manipulate regions closer to the sample surface. Applying instead subsequently wavelengths in a decreasing order, one can first modify the close-to-surface layers with maximal fill factor, showing maximal red shift of the SP band in the spectra (Section 2.5, the

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Fig.2.12). Then by tuning of the laser radiation towards shorter wavelengths, the deeper regions having a lower fill factor of silver inclusions can be addressed, moving the region where modifications happen away from the sample surface, while the already modified areas remain unchanged.

As the proposed technique of multicolor irradiation gives an opportunity to create the discrete dichroic layers in the composite glass containing silver clusters, there are not obstacles to use multicolor laser pulses with different polarization for production of layered structures with special optical properties. For instance, two fields shown in the top of Fig.5.4 were irradiated at 550 nm and 400 nm with crossed polarizations to each other. Indication of p-polarization corresponds in this case to the direction of the laser polarization at 550 nm, while s-polarization is assigned parallel to the laser polarization at 400 nm. This procedure is changing the original yellow color of the exposed at 400 nm and 550 nm fields on the sample into red (s-polarization) and green (p-polarization), respectively. Furthermore, rotation of the light polarization demonstrates an alternating bleaching of the both irradiated regions (Fig.5.4). At the same time, overlapping area between the irradiated fields represents combination of optical properties of both. Thus, change of the polarization switches the color of the mixed region from green into red. Furthermore, extinction spectra of the irradiated areas (Fig.5.4) demonstrate appearance of the additional absorption bands in right side from original SP resonance with maximum about of 413 nm: at 500 nm after irradiation at 400 nm and at 620 nm after exposure at 550 nm. In both cases, these bands we observed only in polarization parallel to the polarization of laser pulses used for modification. However, overlapping area demonstrates both resonances in mutually perpendicular polarizations (see Fig.5.4). This result is an additional convincing prove of the formation of the independent dichroic layers in the depth upon multicolor irradiation with fs laser pulses.

In addition, as well as in the work of Dr. M. Kaempfe [5.6], we have observed that heating of the sample to approximately 600 °C or re-radiation of modified regions by a cw- or Q-switched laser at 532 nm near to the SP band restores the original extinction spectra, being identical within experimental accuracy with those of the samples before irradiation. This indicates a relaxation of the silver nanoparticles back to their initial, spherical shape. For 532 nm laser irradiation, the laser polarization had to be appropriately aligned for effective excitation of SP band. This results in local heating of the sample over the glass transition temperature and relaxation of modified Ag nanoparticles. Thus, the whole transformation process described here is in principle reversible, and thus the nanostructured materials consisting of metal nanoparticles in glass, in combination with tunable fs or ps laser sources, could potentially be used for very long-lived, but nevertheless rewritable data storage devices. In turn, the next section we will consider an opportunity to use the composite glass with embedded Ag nanoparticles in 3D optical data storage.

## 5.2 Composite glass with Ag nanoparticles as a promising media for 3D optical data storage by spectral coding.

In the last two decades composite materials containing metal nanoparticles found various applications in different fields of science and technology. The fact that the SP strongly depends on the host matrix, shape and distribution of metal nanoparticles [5.1, 5.2, 5.7], allows to use the composite materials in development of novel optical devices with unique linear and nonlinear optical properties. For instance, the dependence of the SP resonance on the shape of Ag nanoparticles was used for optical data storage by spectral coding [5.8-5.9]. In combination with the fs laser assisted shape modification of spherical Ag nanoparticles in glass this method opens up a route for using composite material containing Ag nanoparticles as medium for optical data storage. Moreover, the capacity of the optical data storage devices can be extremely enhanced using multiple wavelengths and multiple coding layers [5.10-5.11]. In turn, in the last section we demonstrated an opportunity to control the depth of the anisotropic modifications in the composite glass with varying fill factor of Ag nanoparticles by attenuation of the excitation wavelength. Moreover, the fs laser induced dichroism in composite glass opens a way to enhance the data capacity using the laser polarization for spectral data coding. Reversibility of the fs laser induced modifications by heating of the sample up to glass transition temperature let us to discuss a creation of the new rewritable 3D optical data storage devices on the basis of the Ag nanoparticles incorporated in glass matrix.

The storage capacity of an optical disk (Fig.5.5) can be expressed as follows

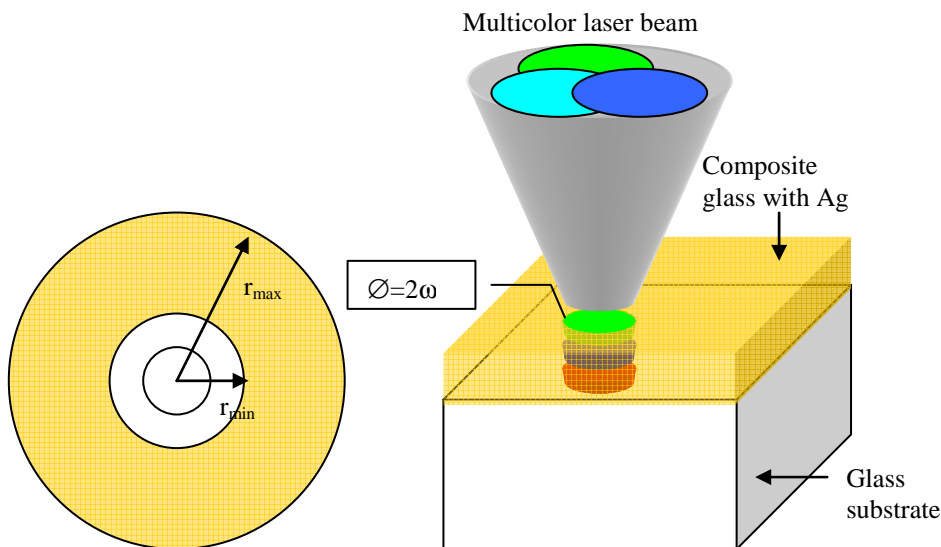


Fig.5.5 Schematic illustration of multiwavelength multilayer optical disc.

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$$C = \frac{NM(r_{\max}^2 - r_{\min}^2)}{\omega^2}, \quad 5.1$$

where  $\omega$  is the spot size of the modified area (storage unit),  $r_{\max}=58$  mm and  $r_{\min}=25$  mm are typical values for the standard CD,  $N$  is a number of the layer used in the storage unit,  $M$  is a number of bits stored in the single layer of the storage unit. According to the Eq.5.1 there are three ways for enhancement of the data capacity of an optical disc: 1) minimization of the size of the modified region (storage unit); 2) usage of the multilayer structures; 3) increase of a number of logical states in the single layer of the storage unit.

Hence, in this part of my thesis we will show a principle, which could be used for creation of high density 3D optical data disc on the basis of composite glass with embedded Ag nanoparticles.

5.2.1. Effect of the peak pulse intensity on the spot size of the modified area in composite glass with Ag nanoparticles.

Since invention of the first optical CD in 1981 and development of the first CD-ROM in 1985 by Philips and Hitachi the optical storage technology stirred much interest of many researcher groups and manufacturers working on enhancement of the data storage capacity of novel optical storage media. A drastic increase of the data capacity of the recent developed optical discs in the last decade was mainly achieved by minimization of the size of burned defect in the active layer as well as by reduction of the gap between burned bits. Moreover, since writing technique is based on thermal effects induced in the active layer by CW lasers, the size of the stored bits is defined by the diffraction limit of the focused laser beam. In turn, as it has already been discussed in Chapter 2, the spot size (spot radius) of a laser beam can be given as

$$\omega = \frac{\lambda M^2}{\pi \cdot N.A.}, \quad 5.2$$

where  $\lambda$  is the laser wavelength, N.A. is the numerical aperture of a focusing objective,  $M^2$  is the beam quality factor. Thus, shorter laser wavelengths and larger N.A. lead to the decrease of the laser spot size and consequently minimization of the burned bit on the disc. In turn, change of the writing wavelength from 780 nm (CD) to 640 nm (DVD) (Fig.5.6)

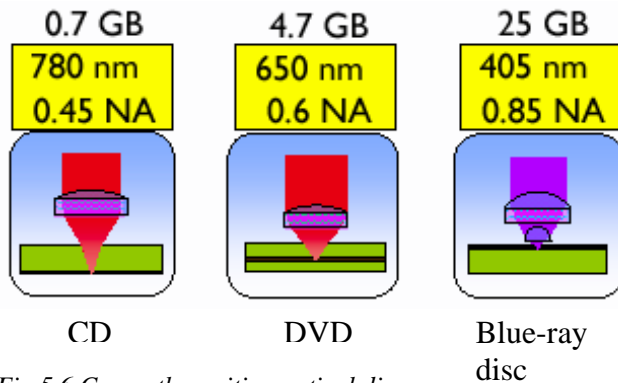


Fig.5.6 Currently exciting optical discs.  
Origin: Ref.[5.12]

allowed to increase the storage capacity from 700 MB on CD up to 4.7GB on DVD. Appearance of the blue laser diodes emitting at 405 nm has facilitated to raise the recording data volume up to 25 GB in so-called Blue-ray discs. Moreover, in October 2004 JVC, also known as Victor Company of Japan, announced that it has

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developed the world's first single lens with a numeric aperture of 0.95. In principle, the new lens can boost the capacity of a 12cm-diameter single-layer disc to more than 40GB of data. However, the diffraction limit is still a main restricting factor for the size of the logical unit.

One of the ways to overcome the diffraction limit is via usage of the intense

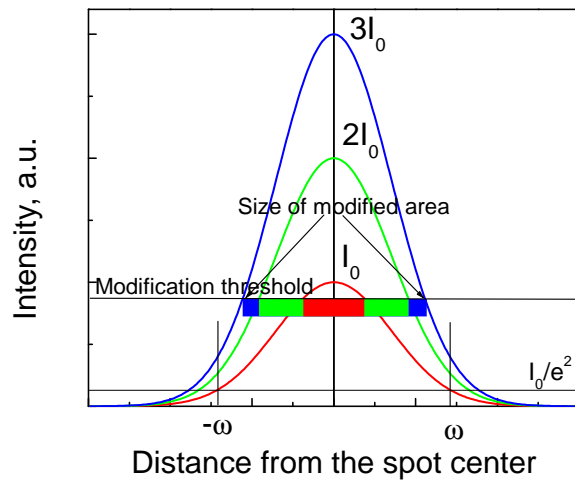


Fig.5.7 Schematic explanation of the size control of modified area by variation of the peak pulse intensity.

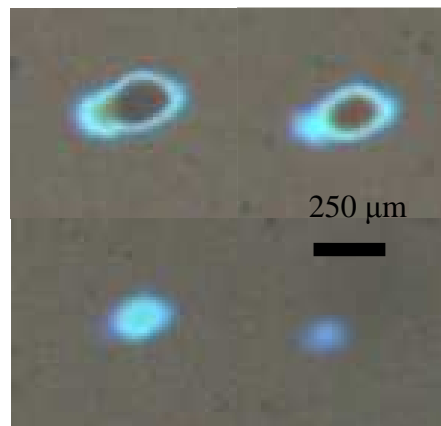


Fig.5.8 Dichroic spots on the sample formed by laser pulses with different peak pulse intensities.

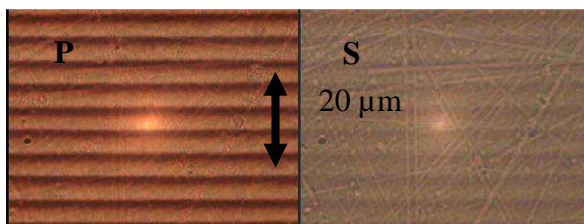


Fig.5.9. Dichroitic grating written in composite glass containing Ag nanoparticles with fs laser pulses at 400 nm.

fs laser pulses and nonlinear processes in the media for recording of information. As a fact, production of 100 nm structures is possible by ablation of chromium film exposed to induced fs laser pulses at 780 nm [5.13]. The idea was to use the peak laser fluence slightly above the ablation threshold. In such case modifications occurs only in the central part of the beam producing sub-diffraction structures.

In Chapter 3 it has been shown that fs laser assisted anisotropic modifications in the composite glass with Ag nanoparticles appear only by overcoming of a certain threshold. Obviously, using pulses with peak intensities slightly above the modification threshold (see Fig.5.7) allows to minimize the modified region in composite glass.

Presented in Fig.5.8 sample was irradiated at 400 nm with 150 fs laser pulses and was actually used to study intensity dependences presented in Chapter 3. The laser beam was focused in the spot with diameter about of 270  $\mu\text{m}$  by the lens with 300 mm focus length (the sample wasn't placed in the focus). Four spots on the sample shown in the Fig.5.8 are corresponding to the pulses with energies 100  $\mu\text{J}$  (2.4  $\text{TW}/\text{cm}^2$ ), 60  $\mu\text{J}$  (1.44  $\text{TW}/\text{cm}^2$ ), 40  $\mu\text{J}$  (0.96  $\text{TW}/\text{cm}^2$ ), 20  $\mu\text{J}$  (0.45  $\text{TW}/\text{cm}^2$ ). As it was predicted by the scheme in the Fig.5.7, decrease of the peak pulse intensity leads to significant reduction of the diameter of the modified region being much smaller as the laser spot width. Moreover, usage of the 15x mirror objective with N.A. = 0.28 allows to



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achieve in our conditions the laser spot size not less as 2  $\mu\text{m}$ . However, appropriate selection of the peak pulse intensity allows to generate modifications in submicron scales. Fig.5.9 presents a dichroic grating with lines width lower as 1  $\mu\text{m}$  and distance of 5  $\mu\text{m}$  obtained in the glass with Ag clusters.

Obviously, optimization of the focusing system and laser beam quality ( $M^2$ ) of the burning system allows to overcome the diffraction limit and to minimize the size of modified region down to wavelength scales.

### 5.2.2. Spectral data coding in composite glass with Ag nanoparticles exposed to fs laser pulses

In previous section we discussed an opportunity to increase the data recording density in the glass containing Ag nanoparticles by minimization of the modified area. On the other hand, the high storage density in optical discs can be achieved by coding of information in several active layers [5.10, 5.11]. In section 5.1 the formation of the discrete anisotropic layers in the glass samples with inhomogeneous distribution of Ag nanoparticles in the depth was demonstrated by exposure to multicolor fs laser pulses. Moreover, the depth of the modified layers is defined by the excitation wavelength. Simplicity of the proposed procedure allows us to suggest this technique for coding of information in anisotropic layers created by fs laser excitation. In this case, the number of wavelengths used for the disc burning defines number of active layers and increases linearly the data capacity. In Section 5.1 we demonstrated irradiation of the samples at tree different wavelength (400 nm, 500 nm and 550 nm). However, there are not visible obstacles to increase a number of incident wavelengths using for example wavelength division of the supercontinuum generated in the photonic crystal fiber [5.14, 5.15]. At the same time, samples used for 3D optical data storage require an optimization of the distribution function of the metal clusters in the depth. Obviously, the ideal medium for such type of the data storage would be a disk with stacked glass layers containing Ag nanoparticles, which differ from each other by filling factor of silver clusters. In this case, each layer excited independently by appropriate wavelength.

In addition, multiplexing of the data in each dichroic layer can be obtained by spectral data coding using the polarization dependence of the SP resonance of ellipsoidal metal nanoparticles [5.8]. In our case, the orientation of the modified Ag

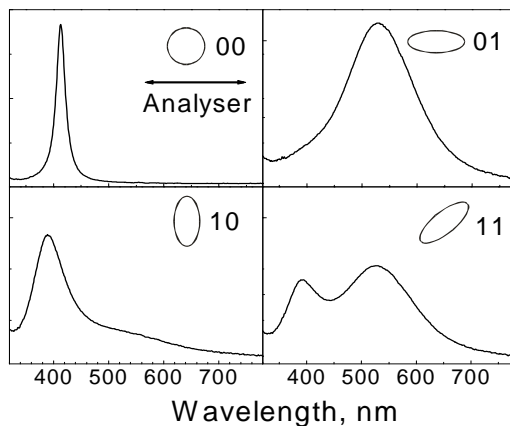


Fig.5.10 Spectral coding of two bits of information by variation of writing laser polarization and shape modification of spherical Ag nanoparticles in glass

nanoparticles embedded in the glass is assigned by direction of the laser polarization during irradiation and can be simply switched during burning process. Thus, by irradiation of a single layer using three different orientations of the laser polarization (angle between the laser polarization and polarization of analyzer is  $0^\circ$ ,  $45^\circ$  and  $90^\circ$ ), it is possible to achieve four independent logic states given by a set of four extinction spectra of modified Ag clusters (see Fig. 5.10). In turn, the spectra were measured by constant polarization direction of the

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analyzer. Obtained set of the four different spectra corresponds with two data bits of the storage unit in the single layer. Using even three wavelengths and three laser polarization directions to exposure the glass sample with filling factor gradient of Ag nanoparticles the storage density of the disc can be enhanced by factor 6. It means that the data capacity of the simple DVDs could be enhanced up to 30 GB, which is higher than modern HD-DVD and Blue-Ray Discs. Appropriate choice of the peak pulse intensity and reduction of the spot size, in addition to increase of the number of wavelengths used for multicolor burning and optimization of the fill factor gradient and usage of discs with several silver containing layers could significantly enhance the capacity of this optical disc.

In addition, as it has already been pointed out, observed fs laser induced modifications in composite glass with Ag nanoparticles are reversible by heating at approximately 600 °C or re-radiation of the modified region by a cw or Q-switched laser at 532 nm near to the SP band. This fact demonstrates a significant advantage of the proposed technique, which allows development of high-density rewritable optical glass discs with embedded metal nanoparticles.

### 5.3. Preparation of high contrast structural polarizer in composite glass with Ag nanoparticle by multicolor fs laser irradiation

In Chapter 3 we considered modification of the single spherical Ag nanoparticles in the soda-lime glass upon exposure to intense fs laser pulses near to the SP resonance. This procedure leads to the laser induced dichroism of the SP bands in extinction spectra caused by the elongation of initially spherical shape of the Ag clusters. Obviously, observed effects could find a broad application in the different fields of science and technology. For instance, in previous section we proposed technique for 3D high density optical data storage using fs laser induced dichroism in the composite glass containing silver clusters. Here it will be shown that fs laser processing of such glass can be used for manufacture of wavelength selective high contrast structured polarizers.

The laser induced dichroism studies in Chapter 3 were carried out on the samples, where the thickness of the glass layer with Ag nanoparticles was less or equal to the laser beam penetration depth. Such optically thin samples allow us to achieve maximal homogeneity of the irradiated region. On the other hand, the low optical density restricted the contrast of the induced dichroism. In order to produce high contrast dichroitic filters we need obviously samples with thick photosensitive layer containing high concentration of Ag nanoparticles. In particular, increase of the fill factor of Ag clusters in the glass allows CORNING and CODIXX AG to produce broad band polarizers with optical density much higher as 3 and the contrast up to  $10^5$  just by mechanical stretching of glass heated up to transition temperature.

On the other hand, the depth of modifications in composite glass with high fraction of silver nanoclusters is restricted by small laser beam penetration in the sample due to high absorption coefficient. Increase of the peak pulse intensity will evoke inhomogeneous modifications of silver clusters in the depth: near to the surface high pulse intensity leads to the destruction of the nanoparticles giving the

isotropic contribution in extinction spectra (see Chapter 3) and minor elongation of Ag clusters in the depth responsible for the observed dichroism. However, this problem can be solved using subsequent modification by multicolor fs laser irradiation. The idea is to use attenuation of the excitation wavelength to modify samples layer by layer in the depth.

For experiments, we used samples with spherical Ag nanoparticles provided by CODIX AG. Irradiation conditions were similar to the case of 3D anisotropic structuring (see Section 5.1): three wavelengths 400 nm, 520 nm and 550 nm were used for

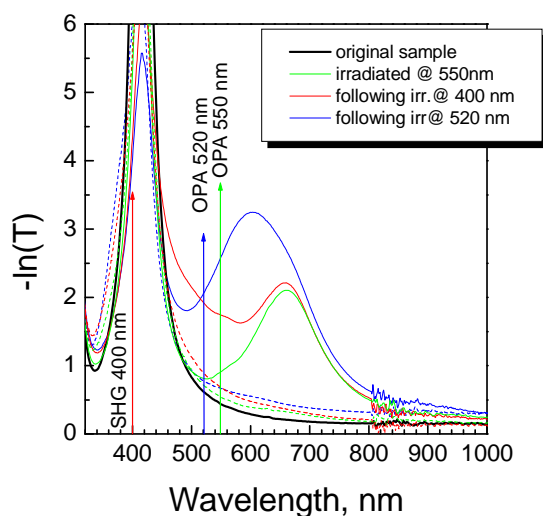


Fig.5.11 Extinction spectra of the composite glass with silver nanoparticles subjected to the multiple irradiation at 400 nm, 520 nm and 550 nm. Solid lines - *p*-polarisation, dotted lines - *s*-polarisation.

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excitation. However, exposure of the samples was carried out from the side with layer containing Ag nanoparticles. The peak pulse intensity was chosen slightly above the modification threshold. This allows to achieve modifications only in thin layer (less than penetration depth).

First, we have exposed the sample to fs laser pulses at 550 nm leading to appearance of an additional absorption band near to 660 nm in p-polarized extinction spectra (Fig.5.11).

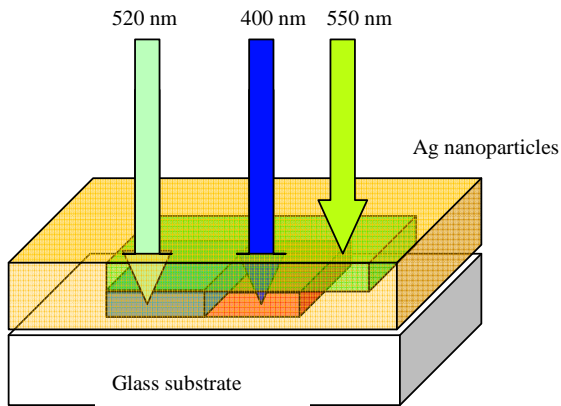


Fig.5.12 Scheme of the preparation of the high contrast dichroic filters by multicolour irradiation of the composite glass with Ag nanoparticles

As it has been shown in the Section 5.1, observed spectral changes can be associated with modification of the Ag nanoparticles with maximal filling factor and distributed near to the surface (Fig.5.12). After that, we irradiated the same area on the sample at 400 nm with the same laser polarization. Since the SP resonance of the nanoparticles in the upper layer is shifted towards longer wavelengths, the penetration depth of the laser pulses at 400 nm increases. Thus, the laser pulses affect on silver clusters

placed in the deeper regions. This results in the following alteration in the extinction spectra indicating additive increase of the absorption between 500 and 600 nm. Scanning of the laser beam through the sample was performed many times until the spectral changes reach a steady state. It means that all the available nanoparticles for laser radiation are modified, and SP band was shifted in red spectral range but the residual absorption obviously prevents excitation of clusters in the depth of the sample. However, as it was found in Chapter 3, deformed by fs laser pulses Ag nanoparticles are able to subsequent modifications induced by excitation at second wavelength coinciding with SP resonance. Hence, irradiated sample was subjected to the following exposure at 520 nm resulting in subsequent particles transformations in recently modified layer responsible for the following shift of the SP resonance to 600 nm and spectral hole burning at 500 nm. In this way the absorption losses at 400 nm can be significantly decreased in modified layers (penetration depth is increased) and deeper regions in the sample become available for the following modification by fs laser pulses at 400 nm. This procedure can be performed many times until modification of whole amount of the nanoparticles in the sample. Using the chosen excitation wavelengths we obtained an dichroic area with absorption maximum in extinction spectra peaked near 600 nm. Moreover, the spectral contrast in the modified area (a ratio between transmittance of the sample in the s- and p-polarizations with extraction of the reflection losses from the glass surface) was calculated to be about 20 at 600 nm. Obviously, using another combination of the excitation wavelengths it's possible to produce filters with appropriate spectral characteristics. It's important to point out, that the thickness of the active layer in these samples was about 6  $\mu\text{m}$ . Since the contrast is exponentially rising with the thickness, increase of the silver containing glass layers will considerably improve the contrast of the dichroic filter produced by exposure to the fs laser pulses.

In conclusion to this chapter, the fs laser induced modifications have been studied in the composite glass with Ag nanoparticles distributed in the depth with

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strong filling factor gradient. It was shown that exposure of such samples to fs laser pulses at various wavelengths can lead to formation of discrete anisotropic layers in the depth. In turn, the distances of the modified layers from the surface as well as spectral properties are defined by the excitation wavelength and local fraction of Ag nanoparticles in the sample. Demonstrated technique opens us an opportunity for 3D microstructuring in the composite glass by means of fs multicolor laser radiation and can be used for various applications. For instance, 3D structuring as well as anisotropic character of the laser induced modification can be used for optical spectral data coding and offer the composite glass with Ag nanoparticles as a promising medium for development of novel optical high density storage devices. Moreover, the strong intensity dependence of the fs laser dichroism and appropriately chosen peak pulse intensity allow to overcome the diffraction limit of the size of burning unit, which will drastically increase the data storage capacity. The main advantage of the composite glass with Ag nanoclusters is that that the heating in oven as well as local heating by exposure to Q-switched or CW lasers near to the SP band result in the reversibility of the fs laser induced modifications. This allows to use this technique for creation of rewriting sources for optical data storage. On other hand, multicolour irradiation of the composite glass with Ag nanoparticles can be effectively used for manufacturing of high contrast structured polarizers and microfilters. Nevertheless, we believe that this approach could find many additional applications in development of different 3D polarization and wavelength selective microdevices such as polarizers, filters, gratings, RGB and DWDM devices, optical and plasmonic embedded circuits.